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Curtis B. Herbert, Ph.D.

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TO: Examiner Patrick Niland
          Group Art Unit 1714

PHONE #:   571-272-1121
FAX #:   571-273-8300

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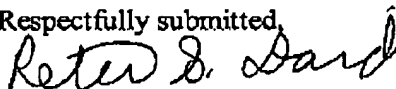
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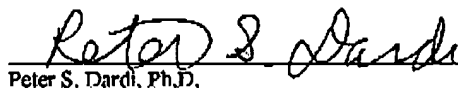PHONE #:   404-949-5730

Attached is the following for filing in the above-identified application.

      (1)   Attachment for Amendment filed August 2, 2006, which was inadvertently not attached with the Amendment.

Respectfully submitted,

Peter S. Dardi, Ph.D.
Registration No. 39,650

CERTIFICATE OF FACSIMILE TRANSMISSION

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September 2, 2006
Date   Peter S. Dardi, Ph.D.

POLYMER CHEMISTRY
An Introduction

SECOND EDITION

Malcolm P. Stevens
University of Hartford

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To Marcia, Jeff, and Phil

9

Reactions of vinyl polymers

9.1 Introduction

The subject of polymer reactions is so broad and the literature so extensive that it is not possible to present more than a survey of the field in a book of this type. Chemical modifications encompass a wide range of applications: ion-exchange resins; polymeric reagents and polymer-bound catalysts; polymeric supports for chemical reactions; degradable polymers to address medical, agricultural, or environmental concerns; flame-retardant polymers; and surface treatments to improve such properties as biocompatibility or adhesion, to name a few. Books and symposia proceedings[1-5] covering reactions of polymers treat individual topics in depth. The purpose of this chapter is to summarize and illustrate chemical modifications of vinyl polymers. For convenience these are grouped into five general categories: (1) reactions that involve the introduction or modification of functional groups, (2) reactions that introduce cyclic units into the polymer backbone, (3) reactions leading to block and graft copolymers, (4) crosslinking reactions, and (5) degradation reactions. Only with polymers in the first category is there no overall change in the gross structure of the polymer.

Before we discuss each type, it should be pointed out that while polymers will, in principle, undergo all the reactions common to low-molecular-weight compounds, contrasting behavior may arise from the polymer's molecular size, shape, or morphology. If a polymer is semicrystalline, for example, the crystalline regions, because of their impermeability, are usually inaccessible to chemical reactants, and reaction may be limited to the amorphous regions. Even in a completely amorphous polymer, not all the functional groups of interest are necessarily equally accessible. Conformational or localized steric effects might well influence the rate or extent of the reaction in different parts of the same molecule. At the same time, the proximity of functional groups might enhance a reaction by the *neighboring group effect*. Copolymers of acrylic acid and *p*-nitrophenyl methacrylate, for example, undergo base-catalyzed hydrolysis faster than simple *p*-nitrophenyl esters because of participation by neighboring carboxylate anions (9.1).[6] That neighboring group-

chemistry.

$$CH_2\text{-}C \quad \longrightarrow \quad (9.1)$$
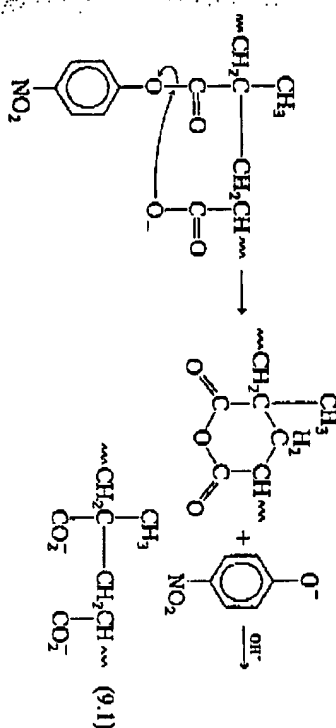
Another complicating factor in polymer reactions is the possibility that the reaction itself might change the physical form of the polymer. Even at low levels of conversion a reaction could alter the polymer's conformation, there-by influencing the reaction rate at unreacted sites; or it might even cause the polymer to precipitate, which would effectively preclude further reaction in the precipitated regions. The possibility that such variables might play a role should be taken into account in effecting any polymer modification.

9.2 Functional group reactions

9.2.1 Introduction of new functional groups

Among the oldest commercial processes are the chlorination (9.2) and chloro-sulfonation (9.3) of polyethylene.[7,8] The properties of polyethylene are substantially altered by chlorination. Flammability is decreased. Solubility is increased or decreased depending on the level of substitution. If the chlorina-tion is run under heterogeneous conditions (polyethylene suspended in an inert medium), the resultant polymer is more crystalline at comparable levels of chlorination than a similar polymer prepared using polyethylene solution. This is not unexpected, because the homogeneous process would distribute the chlorine more randomly. Chlorosulfonation provides sites for subsequent crosslinking reactions. Chlorination of poly(vinyl chloride) is also used
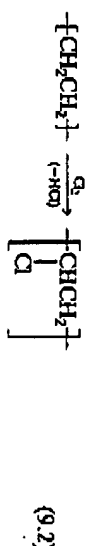
$$\{CH_2CH_2\} \xrightarrow[(-HCl)]{Cl_2} \{CHCH_2\} \quad (9.2)$$
$$\qquad\qquad\qquad\qquad\qquad \mid$$
$$\qquad\qquad\qquad\qquad\qquad Cl$$

$$\{CH_2CH_2\} \xrightarrow[(-HCl)]{Cl_2, SO_2} \{CH_2CH\} \quad (9.3)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad \mid$$
$$\qquad\qquad\qquad\qquad\qquad\qquad SO_2Cl$$

stitution reactions of these types cause crosslinking by radical combination reactions, hence the reaction conditions must be carefully controlled. Both chlorinated and chlorosulfonated polyethylene are, however, available as commercial products of long standing,[9] the latter under the well-known Hypalon (du Pont) trademark.

Fluorination may be accomplished by direct reaction between solid polymer and fluorine.[10] Special techniques such as use of mixtures of nitrogen and fluorine are needed to avoid degradation reactions, but polyethylene can be converted almost quantitatively to the fully fluorinated polymer by this technique. Where double bonds or benzene rings are present in the polymer, both substitution and addition occur. Polystyrene, for example, yields the fully fluorinated saturated polymer on reaction with fluorine (9.4). Where the reaction is particularly useful is in surface fluorination to enhance chemical inertness and—in the case of plastic bottles—to improve solvent barrier properties.[11]

$$\begin{array}{c}-[CH_2CH]-\\ |\\ C_6H_5\end{array} \xrightarrow[(-HF)]{F_2} \begin{array}{c}-[CF_2CF]-\\ |\\ C_6F_{11}\end{array} \qquad (9.4)$$
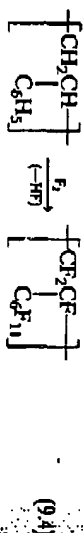
Aromatic substitution reactions (nitration, sulfonation, chlorosulfonation, etc.) occur readily on polystyrene[12,13] and are useful for manufacturing ion-exchange resins or for introducing sites for crosslinking or grafting. Chloromethylation (9.5) of polystyrene is particularly important for introducing new functionalities because the resultant benzylic chloride undergoes nucleophilic displacement so readily. Vinylbenzyl chloride (a mixture of *meta* and *para*) and its polymers are, in fact, available commercially for just such a purpose. The functionalized polymers, crosslinked by including small amounts of divinylbenzene during polymerization, are used for *solid phase synthesis*, in which the insoluble polymer is used as a "handle" for maintaining a catalyst or reaction product in a solid phase for easy separation from the reaction medium.[14-19] A very important example of this technique for synthesizing proteins is described in Chapter 17.

$$\begin{array}{c}-[CH_2CH]-\\ |\\ C_6H_5\end{array} \xrightarrow[AlCl_3]{CH_3OCH_2Cl} \begin{array}{c}-[CH_2CH]-\\ |\\ CH_2Cl\end{array} + CH_3OH \qquad (9.5)$$
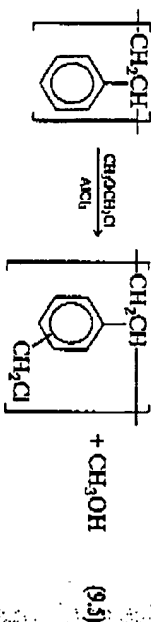
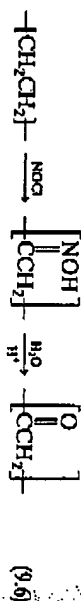Another example that illustrates the value of adding new functionalities is the introduction of ketone groups via the intermediate oxime (9.6) to render polyethylene photodegradable,[20] a process discussed later in the chapter.

$$-[CH_2CH_2]- \xrightarrow{NOCl} \begin{array}{c}[NOH]\\ |\\ -[CH_2]-\end{array} \xrightarrow[H^+]{H_2O} \begin{array}{c}[O]\\ ||\\ -[CH_2]-\end{array} \qquad (9.6)$$

Conversion of one functional group to another is used primarily to obtain polymers difficult or impossible to prepare by direct polymerization. An example is the commercially important synthesis of poly(vinyl alcohol)[21,22] by hydrolysis or alcoholysis of poly(vinyl acetate) (9.7). Poly(vinyl alcohol) cannot be made directly because vinyl alcohol is the unstable enol form of acetaldehyde (see exercise 11, Chapter 1). Isotactic poly(vinyl alcohol) can be prepared by acid cleavage of isotactic poly(vinyl t-butyl ether) (9.8) (the latter made by cationic polymerization of monomer at −78°C).[23]

$$\begin{array}{c}-[CH_2CH]-\\ |\\ OCCH_3\\ ||\\ O\end{array} \xrightarrow[\Delta]{CH_3OH} \begin{array}{c}-[CH_2CH]-\\ |\\ OH\end{array} + CH_3CO_2CH_3 \qquad (9.7)$$

$$\begin{array}{c}-[CH_2CH]-\\ |\\ OC(CH_3)_3\end{array} \xrightarrow{HBr} \begin{array}{c}-[CH_2CH]-\\ |\\ OH\end{array} + BrC(CH_3)_3 \qquad (9.8)$$
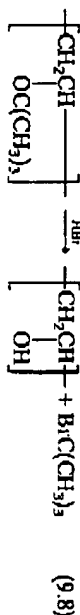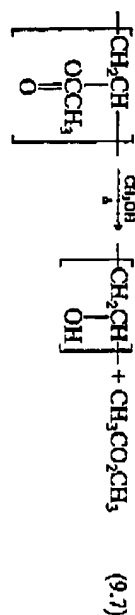
Examples of syntheses of other polymers difficult or impossible to obtain directly are the following:

1. Saponification of isotactic or syndiotactic poly(trimethylsilyl methacrylate) (both prepared under anionic conditions) to yield isotactic or syndiotactic poly(methacrylic acid), respectively (9.9).[24]

$$\begin{array}{c}CH_3\\ |\\ -CH_2C-\\ |\\ C=O\\ |\\ OSi(CH_3)_3\end{array} \xrightarrow[(2)H^+]{(1)H_2O,\,OH^-} \begin{array}{c}CH_3\\ |\\ -CH_2C-\\ |\\ CO_2H\end{array} \qquad (9.9)$$

2. Hofmann degradation of polyacrylamide to give poly(vinyl amine) (9.10),[25] a reaction complicated by side reactions leading to crosslinking.

$$\begin{array}{c}-[CH_2CH]-\\ |\\ CONH_2\end{array} \xrightarrow{Br_2,\,OH^-} \begin{array}{c}-[CH_2CH]-\\ |\\ NH_2\end{array} \qquad (9.10)$$

3. Synthesis of "head-to-head poly(vinyl bromide)" by controlled bromination of 1,4-polybutadiene (9.11).[26]

$$-[CH_2CH=CHCH_2]- \xrightarrow{Br_2} \begin{array}{c}-[CH_2CH-CHCH_2]-\\ |\quad\ |\\ Br\ \ Br\end{array} \qquad (9.11)$$

m-chloro-
perbenzoic
acid

Scheme 9.1. Some functional group conversions of telechelic polyisobutylene. [32]

1. Acetyl sulfate
2. Base

...backbone; in some instances conversion of end groups of telechelic polymers leads to useful products. An example, illustrated in Scheme 9.1, involves dehydrochlorination of chloride-terminated polyisobutylene prepared by the inifer method (Chapter 7). [32] Epoxidation of the resultant vinyl groups with m-chloroperbenzoic acid leads to epoxide-terminated polymer that can be ...ired by reactions analogous to those used with epoxy resins (discussed in Chapter 11). Sulfonation followed by neutralization with base yields a poly-...ther with properties of a thermoplastic elastomer. The elastomeric behavior arises from coulombic attraction of the ionic end groups leading to microdo-mains similar to those exhibited by ABA block copolymers.

9.3 Ring-forming reactions

As might be expected from our earlier consideration of restricted rotation (Chapter 3), the introduction of cyclic units into polymers generally results in greater rigidity, higher glass, transition temperatures, and, frequently, improved thermal stability. One of the most important cyclization reactions leading to high thermal stability is the manufacture of *carbon fiber* (also called *graphite fiber*). * It is not a new process; in the 1870s Edison prepared carbon fiber filaments for his first electric light bulbs by pyrolyzing natural cellulose fibers. Most carbon fiber today is made by controlled pyrolysis of polyacrylo-nitrile fibers. [33-35] This is a complex free radical process involving a series of reactions leading eventually to a highly crosslinked graphitelike polymer [Scheme 9.2] accompanied by loss of HCN and N_2. Quinone-type structures

*While the terms *carbon fiber* and *graphite fiber* are often used synonymously, many workers in the field prefer to reserve the latter for fibers that have been treated at temperatures in excess of MORC, at which point the fibers assume a more truly graphitelike structure.

Other types of "classical" functional group conversions include dehydro-chlorination of poly(vinyl chloride) (9.12) [27] (an early synthesis of polyacet-ylene), hydroformylation of polypentenamer (9.13), [28] and hydroboration of 1,4-polyisoprene (9.14). [29]

(9.11)

(9.12)

(9.13)

(9.14)

A less familiar reaction is the conversion of a fraction of the chloro groups of poly(vinyl chloride) (9.15) for purposes of cross-linking [30,31] (discussed in Section 9.4).

(9.15)

Ladder
graphite-type
polymer

Scheme 9.2. Reactions involved in pyrolysis of polyacrylonitrile to form carbon fiber.

stress, longitudinal order results and the graphite fibers exhibit very high modulus. Such fibers, which may still contain residual nitrogen, are useful primarily in high-strength composites and in applications requiring good heat resistance.

Ladder structures are also formed from poly(methyl vinyl ketone) by intramolecular aldol condensation (9.16).[36] Nonladder structures, on the other hand, result from such reactions as dechlorination of poly(vinyl chloride) (9.17) or intramolecular Friedel-Crafts acylation of styrene–methyl acryloyl chloride copolymer (9.18).[37] These reactions do not go to completion because cyclization occurs randomly, leaving some functional groups

(9.16)

(9.17)

(9.18)

isolated between ring units. Only when the process is reversible can cyclization reaction be made to approach its theoretical limits. Such a case is the formation of cyclic acetal groups by reaction of aldehydes with poly(vinyl alcohol) (9.19) in which more than 90% of the hydroxyl groups can be

(9.19)

converted. This particular reaction is important commercially; the product, when R = C₃H₇, commonly called poly(vinyl butyral), is used as a plastic film in laminated safety glass. Another commercially important cyclization

decrease gas permeability.

Rubber and other diene polymers undergo cyclization in the presence of acid.[39] A probable pathway is shown for cis-1,4-polyisoprene (9.21); however, because of the high probability of transfer reactions occurring, only about one to four rings are fused together in any fused-ring sequence. As might be expected, the polymer loses its elastomeric properties with the introduction of cyclic units.

(9.20)

(9.21)

9.4 Crosslinking

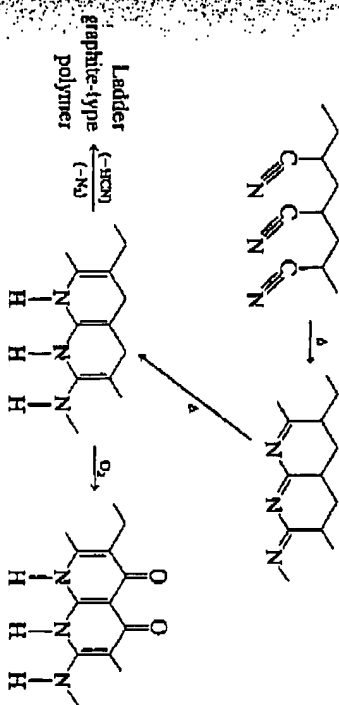From the commercial standpoint, crosslinking is the most important reaction of vinyl polymers and is fundamental to the rubber and elastomer industries. It can be brought about by (1) vulcanization, using peroxides, sulfur, or sulfur-containing compounds; (2) free radical reactions caused by ionizing radiation; (3) photolysis involving photosensitive functional groups; (4) chemical reactions of labile functional groups; or (5) coulombic interactions of ionic species. The physical and morphological consequences of chemical and physical crosslinking are discussed in Chapter 3. Here we are concerned with the reactions leading to chemical crosslinking.

9.4.1 Vulcanization

Vulcanization is a general term applied to crosslinking of polymers, particularly elastomers.[40–43] Peroxide-initiated crosslinking of saturated polymers such as polyethylene proceeds by hydrogen abstraction by radicals resulting from homolytic cleavage of peroxide (9.22) followed by radical combination (9.23). With unsaturated polymers, hydrogen abstraction probably occurs at the allylic position (9.24) with subsequent crosslinking again resulting from radical combination (9.25). It is apparent that addition-transfer processes

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(9.26, 9.27) can also cause crosslinking, because in many instances considerably more crosslinks are formed than would be expected on the basis of only abstraction-combination reactions. Not all vinyl polymers are crosslinkable with peroxides; polypropylene and poly(vinyl chloride), for example, undergo degradation in preference to crosslinking.

$$RO\cdot + \sim CH_2CH_2\sim \longrightarrow \sim \dot{C}HCH_2\sim + ROH \qquad (9.22)$$

$$\sim \dot{C}HCH_2\sim \\ + \\ \sim \dot{C}HCH_2\sim \longrightarrow \sim CHCH_2\sim \atop \sim CHCH_2\sim \qquad (9.23)$$

$$\sim CH_2CH=CHCH_2\sim + RO\cdot \longrightarrow \sim \dot{C}HCH=CHCH_2\sim + ROH \qquad (9.24)$$

$$\sim \dot{C}HCH=CHCH_2\sim \longrightarrow \sim CHCH=\dot{C}HCH_2\sim \qquad (9.25)$$

$$\sim \dot{C}HCH=CHCH_2\sim \\ + \\ \sim CH_2CH=CHCH_2\sim \longrightarrow \sim CHCH=CHCH_2\sim \atop \sim CH_2CH=CHCH_2\sim \qquad (9.26)$$

$$\sim \dot{C}HCH=CHCH_2\sim \\ + \\ \sim \dot{C}HCH=CHCH_2\sim \longrightarrow \sim CHCH=CHCH_2\sim \atop \sim CH_2CH—CH_2CH_2\sim \qquad (9.27)$$
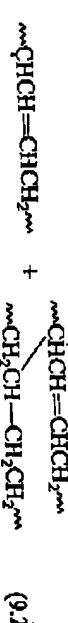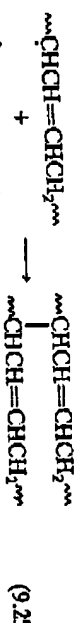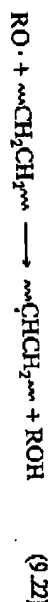
The oldest method of vulcanization, discovered independently in 1839 by Goodyear in the United States and MacIntosh and Hancock in Great Britain, uses elemental sulfur. The mechanism appears to be ionic in nature, involving addition to a double bond to form an intermediate sulfonium ion (9.28) which then abstracts a hydride ion (9.29) or donates a proton (9.30) to form new

$$\sim CH_2CH=CHCH_2\sim + \overset{\delta+}{\sim}S—S\overset{\delta-}{\sim} \longrightarrow \sim CH_2CH—\overset{+}{CH}CH_2\sim + \sim S^- \qquad (9.28)$$

$$\sim CH_2CH=CHCH_2\sim \\ + \\ \sim CH_2CH—\overset{+}{CH}CH_2\sim \longrightarrow \sim CH_2CH—CH=CH\sim + \sim CH_2CH_2—\overset{+}{CH}CH_2\sim \qquad (9.29)$$

$$\sim CH_2CH—CH=CH\sim + \sim CH_2CH—\overset{+}{CH}CH_2\sim \qquad (9.30)$$
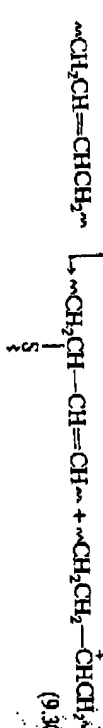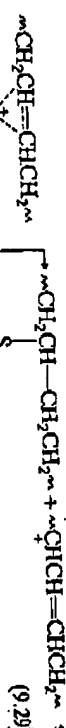
Reactions of Vinyl Polymers 305

cations for propagating the reaction. Termination occurs by reaction between sulfenyl anions and carbocations. Studies on model compounds indicate that, in addition to simple monosulfide or disulfide linkages, some polysulfide groups and cyclic monosulfide groups resulting from intramolecular addition of pendant sulfur to a double bond are also present.

The rate of vulcanization with sulfur can be, and normally is, increased by addition of accelerators such as zinc salts of dithiocarbamic acids (1) or organosulfur compounds such as tetramethylthiuram disulfide (2). Other compounds, notably zinc oxide and stearic acid, are also added as activators.

$$[(CH_3)_2N\overset{\overset{S}{\parallel}}{C}S^-]_2Zn^{2+} \qquad (CH_3)_2N\overset{\overset{S}{\parallel}}{C}S—S\overset{\overset{S}{\parallel}}{C}N(CH_3)_2$$

1   2

Although the mechanism of acceleration is not well understood, acceleration is known to decrease the number of cyclic monosulfide groups and increase the number of monosulfide and disulfide crosslinks.
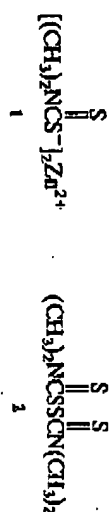
9.4.2 Radiation crosslinking

When vinyl polymers are subjected to ionizing radiation, whether it be photons, electrons, neutrons, or protons, two main types of reaction occur—crosslinking and degradation.[44-48] Generally, both occur simultaneously, although degradation predominates with high doses of radiation. With low doses the polymer structure determines which will be the major reaction. Generally disubstituted polymers tend to undergo chain scission, with monomer being a major degradation product. Thus, such polymers as poly(α-methylstyrene), poly(methyl methacrylate), or polyisobutylene will decrease in molecular weight on exposure to radiation. Halogen-substituted polymers, such as poly(vinyl chloride), break down with loss of halogen. With most other vinyl polymers, crosslinking predominates. A limitation of radiation crosslinking is that radiation does not penetrate very far into the polymer matrix; hence the method is primarily used with films.

The mechanism of crosslinking is free radical in nature and probably involves initial ejection of a hydrogen atom (9.31), which, in turn, removes another hydrogen atom from an adjacent site on a neighboring chain (9.32). Crosslinking then occurs by radical combination (9.33). This is a reasonable

$$—CH_2CH_2— \overset{h\nu}{\longrightarrow} —\dot{C}HCH_2— + H\cdot \qquad (9.31)$$

$$—CH_2CH_2— + H\cdot \longrightarrow —\dot{C}HCH_2— + H_2 \qquad (9.32)$$
$$\text{(neighboring chain)}$$

$$—\dot{C}HCH_2— \\ + \\ —\dot{C}HCH_2— \longrightarrow —CHCH_2— \atop —CHCH_2— \qquad (9.33)$$
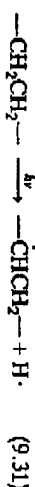
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assumption because hydrogen is a major side product, and random formation of radicals would not give the efficiency of crosslinking that is generally observed.

Chain branches are also ejected. Low-density polyethylene, for example, gives larger amounts of gaseous hydrocarbons on irradiation than does linear high-density polyethylene. Fragmentation reactions of this type, as well as ejection of hydrogen, also lead to double bonds in the polymer chains (9.34) in addition to crosslinking.

$$-CH_2CH- \longrightarrow -CHCH- + H\cdot \longrightarrow -CH=CH- + RH \quad (9.34)$$
$$\qquad\quad R \qquad\qquad\qquad R$$

Radiolysis effects on numerous vinyl polymers have been studied, but polyethylene is most important. Irradiated polyethylene film is used commercially because of its improved tensile and thermal properties. Polystyrene is quite resistant to radiation, a characteristic of aromatic polymers in general, but it can be crosslinked with higher doses.
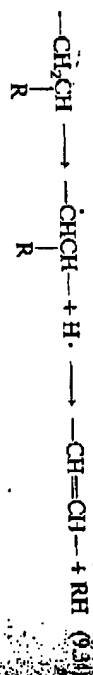
9.4.3 *Photochemical crosslinking*

Ultraviolet or visible light-induced crosslinking[49,50] (*photocrosslinking*) has taken on increasing importance in recent years. Among the numerous applications are printed circuits for electronic equipment; printing inks; coatings for optical fibers; varnishes for paper and carton board; finishes for vinyl flooring, wood, paper, and metal; and curing of dental materials. Photocrosslinking applied to photoresist technology is described in Chapter 4. There are two basic methods for bringing about photocrosslinking: (1) incorporating photosensitizers into the polymer, which absorb light energy and thereby induce formation of free radicals, and (2) incorporating groups that undergo either *photocycloaddition* reactions or light-initiated polymerization.

When triplet sensitizers such as benzophenone are added to polymer, absorption of ultraviolet results in $n \rightarrow \pi^*$ excitation of the sensitizer followed by hydrogen abstraction from the polymer to yield radical sites available for crosslinking by combination reactions. If the chromophore is built into the polymer backbone, as with polymers or copolymers of vinyl ketones, then degradation occurs, either by α-cleavage of the excited polymer (9.35) or by abstraction of a γ-hydrogen (9.36). The former leads to active sites for crosslinking, while the latter results in chain cleavage. (Recall the discussion of Norrish type II reactions in Chapter 4, Section 4.7.) Poly(vinyl esters) undergo analogous α-cleavage reactions (9.37) with subsequent crosslinking. Copolymers of vinyl esters and fluorinated monomers that can be crosslinked by ultraviolet have been developed for use as weather-resistant wood coatings. In this application, the vinyl ester constitutes about 10% of the copolymer and benzophenone is added as a sensitizer.
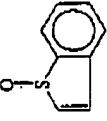
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$$(9.35)$$
$$(9.36)$$
$$(9.37)$$
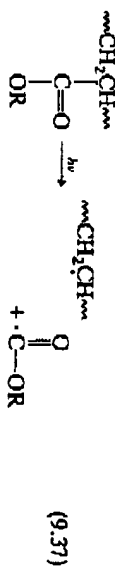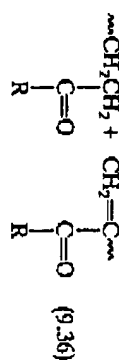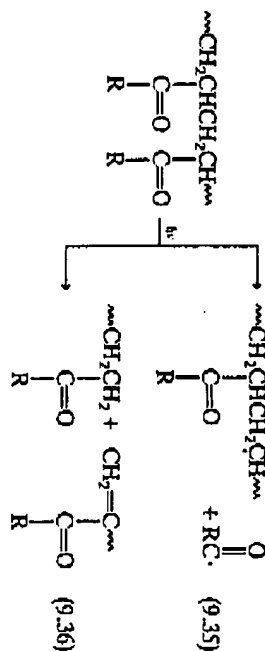
As is the case with radiolysis, polymers prepared from 1,1-disubstituted monomers undergo more extensive degradation, particularly to monomer, on photolysis.

A wide variety of functional groups has been used to effect photocycloaddition or light-induced polymerization crosslinking.[49-56] Many of them are listed in Table 9.1. The groups may be present as part of the backbone or,

Table 9.1. Groups used to effect photocrosslinking[49-56]

Type	Structure
Alkyne	R—C≡C—R
Anthracene	
Benzothiophene dioxide	
Chalcone	ArCH=CHCAr
Cinnamate	ArCH=CHCO$_2$R
Coumarin	

(continues)

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9.4.4 Crosslinking through labile functional groups

Reaction between appropriate difunctional or polyfunctional reagents with labile groups on the polymer chains can bring about crosslinking, but such reactions have not been exploited nearly as much as the more convenient vulcanization methods.

Polymers containing acid chloride groups, such as the previously described chlorosulfonated polyethylene (9.3), react with diamines (9.40) or diols (9.41) to yield sulfonamide and sulfonate crosslinks, respectively.[57] Dihalogen compounds can be used to crosslink polystyrene by the Friedel–Crafts reaction (9.42).[58]

$$(9.40)$$

$$(9.41)$$

$$(9.42)$$
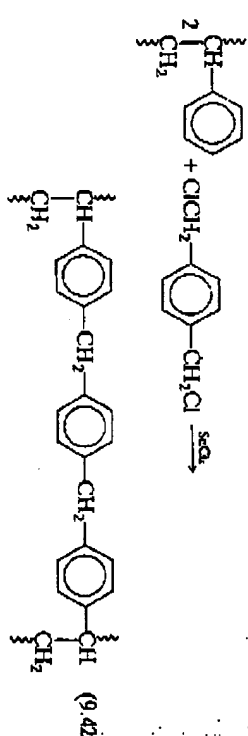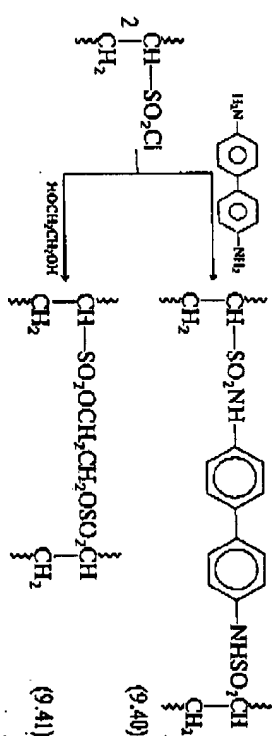
An interesting cycloaddition process has been used to crosslink copolymers of 2-phenyl-5-(4'-vinyl)phenyltetrazole (5) and acrylonitrile. The functional groups remain intact during free radical copolymerization, but on heating the tetrazole ring decomposes and cycloaddition with nitrile occurs to give triazole crosslinks (9.43).[59]

A particularly interesting example of cycloaddition crosslinking involves the Diels–Alder reaction of cyclopentadiene-substituted polymer (see reaction 9.15). It is well known that cyclopentadiene dimerizes by Diels–Alder cycloaddition, one ring acting as diene, the other as dienophile. At about 180°C the dimer reverts to monomer. Cyclopentadiene substituent groups on polymers undergo an analogous reaction, yielding crosslinked polymer by cycloaddition and linear polymer by retrograde Diels–Alder reaction of the

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$$(9.43)$$
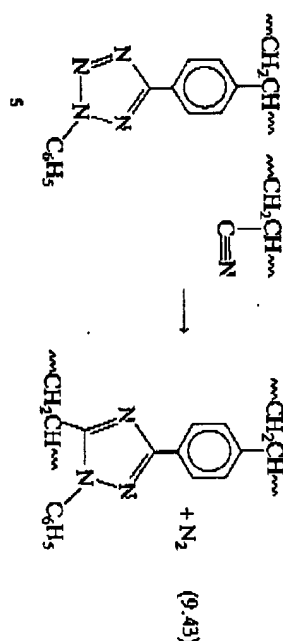
crosslinked polymer at elevated temperatures (9.44).[30] Such reversible systems have potential as thermoplastic elastomers.

$$(9.44)$$

9.4.5 Ionic crosslinking

Examples of ionic crosslinking are the hydrolysis of chlorosulfonated polyethylene with aqueous lead oxide (9.45) to yield lead sulfonate crosslinks, and the partial conversion of poly(ethylene-co-methacrylic acid) (6) to salts of divalent metals. The latter type, marketed under the du Pont trade name Surlyn, are called ionomers.[60,61] (Commercial products may contain univalent as well as divalent metal salts.)

$$(9.45)$$

Ionomers have interesting properties compared with the nonionized copolymer. Introduction of ions causes disordering of the semicrystalline structure, which makes the polymer transparent. Crosslinking gives the polymer

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elastomeric properties, but it can still be molded at elevated temperatures. In fact, molding is generally facilitated by a broader melt range than is the case with the nonionic polymer. Ionic polymers, therefore, also qualify as thermoplastic elastomers. Increased polarity also improves adhesion. Ionomers are used as coatings, as adhesive layers for bonding wood to metal, as blow-molded and injection-molded containers, as golf ball covers, and as blister packaging material. Because of its adhesive qualities, an ionic acrylic copolymer is used as a binder for aluminosilicate dental fillings.

9.5 Block and graft copolymer formation

In Chapters 7 and 8 we encountered the living polymer method of forming block copolymers. In this section we explore some other methods of preparing block copolymers and, for the first time, a few of the numerous procedures developed for preparing graft copolymers.[62-65]

9.5.1 Block copolymers

Polymers containing functional end groups are generally amenable to forming block copolymers.[66] Styrene polymerized with the H_2O_2–$FeSO_4$ redox system, for example, forms hydroxy-terminated polystyrene. Subsequent reaction with an isocyanate-terminated polymer yields an AB block copolymer via urethane linkages (9.46). Similarly, telechelic polymers (functional groups at both ends) can be converted to ABA block copolymer or, if both homopolymers are telechelic, to the $+AB+$ type.

$$\text{\textasciitilde\textasciitilde CHCH}_2\text{OH} + \text{OCN\textasciitilde\textasciitilde} \longrightarrow \text{\textasciitilde\textasciitilde CHCH}_2\text{—OCNH\textasciitilde\textasciitilde} \qquad (9.46)$$

It is worth noting that polymers containing reactive functional groups are, in a sense, "living," and their conversion to block copolymers might be considered in the same light as the living polymer method of creating block copolymers discussed in the previous two chapters.

More recently, block copolymers have yielded to mixed mechanism techniques[67]; that is, the first block is formed by one mechanism (e.g., anionic), and the second by a different mechanism (cationic, free radical, etc.) A schematic representation of an anionic-cationic mixed mechanism synthesis is given in reaction (9.47).

$$xM_1 \xrightarrow{\text{BuLi}} \text{Bu}+M_1+_{x-1}M_1^-\!:\!^-Li^+ \xrightarrow{\text{Br}_2} \text{Bu}+M_1+_{x-1}M_1,\text{Br} \xrightarrow{\text{AgClO}_4}$$
$$\text{Bu}+M_1+_{x-1}M_1^+\text{ClO}_4^- \xrightarrow{yM_2} \text{Bu}+M_1+_x+M_2+_{y-1}M_2^+\text{ClO}_4^- \qquad (9.47)$$

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Peroxide groups introduced to polymer chain ends can be used to initiate a new chain.[65a] Typically an initiator such as the monohydroperoxide of diisopropylbenzene is used, and the resultant polymer (7), which contains an isopropylbenzene end group, can itself be converted to hydroperoxide (9.48).

$$\text{\textasciitilde\textasciitilde CHCH}_2\text{OC—R} \xrightarrow{O_2} \text{\textasciitilde\textasciitilde CHCH}_2\text{OC—R} \qquad (9.48)$$

Addition of a second monomer followed by redox or thermal decomposition of the hydroperoxide initiates polymerization at the chain end. Similarly peroxide units can be formed in a polymer backbone by polymerizing a monomer in the presence of small amounts of oxygen (9.49). Thermal cleavage of the peroxide leads to radical-terminated chains capable of initiating a second monomer (9.50).

$$2x\text{CH}_2\!=\!\text{CH} + O_2 \xrightarrow{\text{initiator}} \left[\text{CH}_2\text{CH}\right]_x\!\!-O-O-\!\!\left[\text{CH}_2\text{CH}\right]_x \qquad (9.49)$$

$$\left[\text{CH}_2\text{CH}\right]_x\!\!-O-O-\!\!\left[\text{CH}_2\text{CH}\right]_x + 2y\text{CH}_2\!=\!\text{CHY} \longrightarrow$$

$$2\left[\text{CH}_2\text{CH}\right]_x\!\!-O-\!\!\left[\text{CH}_2\text{CH}\right]_y \qquad (9.50)$$

Another way to form chain-end radicals is by mechanical degradation of homopolymers using ultrasonic radiation or high-speed stirring.[63] Polyethylene-*block*-polystyrene, for example, has been made by masticating polystyrene in the presence of ethylene. Mastication of mixtures of homopolymers yields similar results. Ionizing radiation may also be used to effect chain cleavage; however, this is more readily applicable to formation of graft copolymers.

9.5.2 Graft copolymers

There are three general methods of preparing graft copolymers: (1) A monomer is polymerized in the presence of a polymer with branching resulting from chain transfer. (2) A monomer is polymerized in the presence of a polymer having reactive functional groups or positions that are capable of being activated, for example, by irradiation. (3) Two polymers having reactive functional groups are coreacted. Chain transfer grafting will be considered first.

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Three components are necessary for grafting by chain transfer: polymer, monomer, and initiator. The function of the initiator is either to polymerize monomer to form a polymeric radical, ion, or coordination complex which can then attack the original polymer, or to react with the original polymer to form such species on the backbone, which initiate polymerization of monomer. As with ordinary copolymerization, it is necessary to consider reactivity ratios of monomers to ensure that grafting will occur. It is also necessary to take into account the frequency of transfer to determine the number of grafts. Normally, mixtures of homopolymers result along with graft copolymer.

Grafting generally occurs at sites that are susceptible to transfer reactions, such as at carbons adjacent to double bonds in polydienes or on carbons adjacent to carbonyl groups. An example of the latter is the reaction of poly(vinyl acetate) with ethylene using a free radical initiator.[57] This particular poly(vinyl acetate)-*graft*-polyethylene and long-product to give a mixture of poly(vinyl alcohol)-*graft*-polyethylene and long-chain carboxylic acids. Grafting efficiency is improved if a group that undergoes radical transfer readily, such as a mercaptan, is incorporated into the polymer backbone.

(9.51)

Cationic chain transfer grafting occurs when styrene is polymerized with BF₃ in the presence of poly(p-methoxystyrene) (9.52).[68,69] In this case the activated benzene rings undergo Friedel-Crafts attack by the carbocationic chain end of polystyrene. Isobutylene, which might be expected to behave similarly, fails to form graft copolymer under these conditions.

(9.52)

Examples of grafting involving activation of functional groups are the following:

1. Synthesis of poly(vinyl chloride)-*graft*-(cis-1,4-polybutadiene) by cationic
···· of butadiene with a diethylaluminum chloride-cobalt complex

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(9.53)

2. Synthesis of poly(p-chlorostyrene)-*graft*-polyacrylonitrile by anionic initiation of acrylonitrile using naphthalenesodium in the presence of poly(p-chlorostyrene) (9.54).[71,72] A polymeric anion radical is the initiating species.

(9.54)

3. Synthesis of 1,4-polybutadiene-*graft*-(isotactic polypropylene) by activation of the polybutadiene with diethylaluminum hydride and TiCl₃ followed by Ziegler-Natta polymerization of propylene (9.55).[73]

(9.55)

Grafts need not be of the vinyl type. Hydrolyzed poly[styrene-*co*-(vinyl acetate)], for example, can be grafted with polyether by reaction with ethylene oxide (9.56).[74]

(9.56)

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without added photosensitizer, or with ionizing radiation, particularly the latter. Free radical reactions are involved in all cases. A major difficulty is that irradiation causes substantial amounts of homopolymerization along with grafting. This has been obviated to some extent by preirradiating the polymer prior to addition of the new monomer. One method is to preirradiate the polymer in the presence of air or oxygen to form hydroperoxide groups on the backbone. Subsequent addition of monomer and heating results in radical polymerization at the peroxide sites accompanied by some homopolymerization initiated by the hydroxy radicals formed on homolysis of hydroperoxide. Preirradiation can also be performed in the absence of air to form free radicals trapped in the viscous polymer matrix. Monomer is then added. The method is not very efficient because of the low concentration of radicals that can be trapped, and homopolymerization can still occur by chain transfer reactions.

Direct irradiation of monomer and polymer together has been most extensively used. Because homopolymerization can occur, monomer and polymer must be chosen carefully. Generally, the best combination is a polymer that is very sensitive to radiation—that is, one that forms a high concentration of radicals—and a monomer that is not very sensitive. Sensitivity is normally measured in terms of G values, which represent the number of free radicals formed per 100 eV of energy absorbed per gram.[47] According to these data, a good combination would be poly(vinyl chloride) and butadiene. Homopolymerization may be reduced by providing radiation in bursts while monomer is allowed to diffuse through the polymer. Irradiation grafting of polymer emulsions is also an effective way to minimize homopolymerization, since the reaction medium remains fluid even at high conversions.

Another method of irradiation grafting involves irradiating an intimate mixture of homopolymers. Apart from the fact that most polymers are

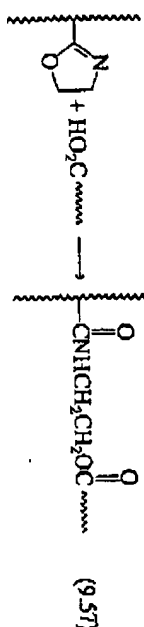Table 9.2. Approximate G values of monomers and polymers[a]

Monomer	G	Polymer	G
Butadiene	Very low	Polybutadiene	2.0
Styrene	0.70	Polystyrene	1.5–3
Ethylene	4.0	Polyethylene	6–8
Acrylonitrile	5.0–5.6	—	—
Methyl methacrylate	5.5–11.5	Poly(methyl methacrylate)	6–12
Methyl acrylate	6.3	Poly(methyl acrylate)	6–12
Vinyl acetate	9.6–12.0	Poly(vinyl acetate)	6–12
Vinyl chloride	10.0	Poly(vinyl chloride)	10–15

[a]Data from Marvel, Sample, and Roy.[22] G values refer to number of free radicals formed per ...

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incompatible, this technique is of limited use, since crosslinking between like polymer chains can occur with equal probability.

The third type of grafting process is exemplified by reactions of oxazoline-substituted polystyrene (a commercial product). The oxazoline group forms addition compounds with a variety of other functional groups including carboxylic acid, anhydride, alcohol, amine, epoxide, mercaptan, and phenol. Grafting of an oxazoline-substituted polymer with a carboxyl-terminated polymer is shown in reaction (9.57). Such grafting reactions can be used, for example, for compatibilizing polymer blends, or for improving surface adhesion between polystyrene molded parts and appropriately functionalized surface coatings.

$$\text{(oxazoline)} + HO_2C\text{\textasciitilde\textasciitilde} \longrightarrow \text{\textasciitilde\textasciitilde}CNHCH_2CH_2OC\text{\textasciitilde\textasciitilde} \tag{9.57}$$

9.6 Polymer degradation

Stability of polymers is of critical interest to manufacturers, and, understandably, polymer degradation reactions have received considerable attention.[75–78] There are three principle methods of degrading polymers: (1) chemical, (2) thermal, and (3) radiative. In addition one can use ultrasonic radiation or mechanochemical techniques (for example, mastication) as described in the previous section.
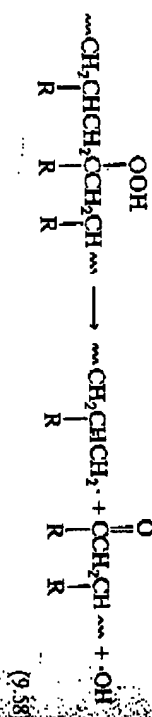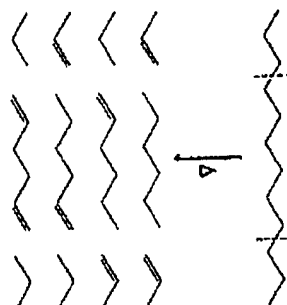
9.6.1 Chemical degradation

This discussion is limited to reactions that cause breakdown of the polymer backbone; it does not cover reactions involving pendant groups. Because the backbones of vinyl polymers are made up of carbon chains containing no functional groups other than the double bonds of diene polymers, chemical degradation is essentially limited to oxidation. Most important is oxidation with oxygen because this has a direct bearing on polymer durability.

Saturated polymers are degraded very slowly by oxygen, and the reaction is autocatalytic. It can be speeded up considerably by application of heat or light or by the presence of certain impurities that catalyze the oxidation process. Tertiary carbon atoms are most susceptible to attack, and this is reflected in the following order of resistance to oxidation of three common polymers: polyisobutylene > polyethylene > polypropylene. Reaction products are numerous and include water, carbon dioxide, carbon monoxide, hydrogen, and alcohols. Crosslinking always accompanies degradation. It is believed
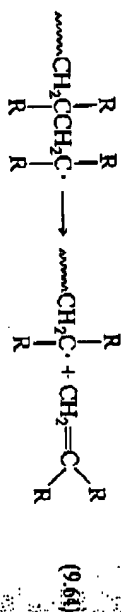
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$$\text{CH}_2\text{CHCH}_2\overset{\overset{\displaystyle OOH}{|}}{\text{CH}}\sim \longrightarrow \sim\text{CH}_2\text{CHCH}_2\cdot + \overset{\overset{\displaystyle O}{\|}}{\text{CCH}_2}\text{CH}\sim + \cdot\text{OH}$$

$$\text{(9.58)}$$

Unsaturated polymers undergo oxidative degradation much more rapidly by complex free radical processes involving peroxide and hydroperoxide intermediates. Allylic carbon atoms are most sensitive to attack, because resonance-stabilized radicals are formed. Oxidation is inhibited in commercial polymers by addition of antioxidants of the type discussed in Chapter 4 (Section 4.9).

Unsaturated polymers are also very susceptible to attack by ozone. Degradation by ozonolysis is discussed in Chapter 4 (Section 4.6). The discussion will not be repeated here except to remind the reader that an effective strategy for improving ozone resistance is to position the alkene moiety that is necessary for crosslinking such that oxidative bond cleavage causes no reduction in molecular weight. Also discussed in Chapter 4 (Section 4.7) are approaches to *enhancing* the oxidative degradability of vinyl polymers by incorporating enzyme-sensitive polymers such as starch or cellulose to promote oxidation by soil microorganisms.

9.6.2 Thermal degradation

There are basically three types of thermal degradation reactions for vinyl polymers[77-79]: (1) *nonchain scission*, (2) *random chain scission*, and (3) *depropagation*. Nonchain scission refers to reactions involving pendant groups that do not break the polymer backbone. Typical of such reactions are dehydrochlorination of poly(vinyl chloride) (9.12), elimination of acid from poly(vinyl esters)—for example, poly(vinyl acetate) (9.59)—and elimination of alkene from poly(alkyl acrylate)s (9.60). The first two reactions lead to highly colored residues, indicating that the double bonds formed in the

$$\text{―[CH}_2\text{CH]―} \longrightarrow \text{―[CH=CH]―} + \text{HOCCH}_3 \quad (9.59)$$

$$\text{―[CH}_2\text{CH]―} + \text{CH}_2\text{=CHR} \quad (9.60)$$

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polymer backbone are primarily conjugated. Enough side reactions occur, however, that decomposition of initially formed hydroperoxide groups is mainly responsible for chain scission (9.58).

...that such elimination reactions are not satisfactory for synthesizing polyacetylene. Nonchain scission has, however, been used as one approach to solving the problems of polyacetylene's intractability[80-83]. The method involves synthesis of a reasonably stable, tractable precursor polymer that can be purified and fabricated, then converted thermally to polyacetylene. An example involves the tricyclic monomer (8), which undergoes metathesis polymerization to precursor polymer (9) (9.61). Thermal degradation of films of the latter (9.62) yields coherent films of polyacetylene. Developed at the University of Durham, this particular approach to making polyacetylene is referred to as the "Durham route."

$$\text{(9.61)}$$

$$\text{(9.62)}$$

Nonchain scission reactions are useful for characterizing copolymers when the amount of a volatile degradation product can be correlated with the concentration of a given repeating unit[84,85] (see Chapter 5, Section 5.5).

Random chain scission results from homolytic bond-cleavage reactions at weak points in the polymer chains. Complex mixtures of degradation products are formed, the origin of which may be explained in terms of radical transfer reactions such as (9.63). It may be recalled (Chapter 5, Figure 5.19) that a gas chromatographic pyrogram of polyethylene exhibits a homologous series of triplet peaks corresponding to alkane, 1-alkene, and α, ω-dialkene, with the largest peak in each triplet being that of 1-alkene. This follows from the breakdown pattern shown in Scheme 9.4. Random chain scission occurs with all vinyl polymers to varying degrees, but it occurs less with increasing substitution on the polymer backbone.

$$\sim\text{CH}_2\text{CH}_2\text{CH}_2 \longrightarrow \sim\text{CH}_2\text{CH}_2 + \cdot\text{CH}_2\text{CH}_2\sim \longrightarrow$$
$$\sim\text{CH=CH}_2 + \text{CH}_3\text{CH}_2\sim \quad (9.63)$$

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Scheme 9.4. Random chain scission of polyethylene.

Depropagation, or depolymerization (unzipping), to give monomer occurs mainly with polymers prepared from 1,1-disubstituted monomers. Initiation may be at a chain end or at a random site along the backbone. Poly(methyl methacrylate) appears to begin unzipping primarily at the chain ends, whereas poly(α-methylstyrene) does so at random sites along the chain. In both cases tertiary radicals are formed with each depropagation step (9.64). Polymers having single substituents on alternate carbons degrade by both depropagation and random chain scission, with the amount of monomer formed varying with temperature.[86]

$$\text{\textasciitilde\textasciitilde\textasciitilde}CH_2CH_2C\!\!\begin{array}{c}R\\|\\|\\R\end{array} \longrightarrow \text{\textasciitilde\textasciitilde\textasciitilde}CH_2C\!\!\begin{array}{c}R\\|\\|\\R\end{array} + CH_2\!\!=\!\!C\!\!\begin{array}{c}R\\\\R\end{array} \qquad (9.64)$$

9.6.3 *Degradation by radiation*

It was mentioned earlier that radiation may cause both crosslinking or degradation. Which predominates depends on radiation dosage, polymer structure, and temperature.[40,47] Ultraviolet or visible light causes 1,1-disubstituted polymers to degrade to monomer almost exclusively at elevated temperatures, whereas crosslinking and chain scission reactions predominate at room temperature. Other vinyl polymers undergo crosslinking primarily, regardless of temperature. Rearrangements may also occur as a result of homolysis and recombination reactions, especially with diene polymers.[87,88]

Ionizing radiation leads to much higher yields of monomer from 1,1-disubstituted polymers at room temperature. Degradations of this type initiated with electron beams are put to advantage in the manufacture of microcircuits using resist technology. At comparable levels of radiation, polyethylene and monosubstituted polymers undergo mainly crosslinking. All vinyl polymers tend to degrade under very high dosages of radiation.

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Review exercises

1. Write a concise definition of the following terms: (a) depropagation; (b) ionomer; (c) nonchain scission; (d) random chain scission; (e) vulcanization.
2. Write equations for the expected reaction of polystyrene with (a) HNO$_3$/H$_2$SO$_4$;